What is claimed is:

1. A method for electrolytic copper plating on a substrate comprising the steps of providing an electrolytic copper plating solution, and contacting the electrolytic copper plating solution with ozone, wherein the electrolytic copper plating solution comprises a compound comprising the formula of –X-S-Y-, wherein X and Y are independently chosen from hydrogen atom, carbon atom, sulfur atom, nitrogen atom, and oxygen atom, and X and Y may be the same only when they are a carbon atom.

2. The method of claim 1, wherein the compound comprising the formula –X-S-Y- is chosen from compounds of formulas (1) to (8)

(1) $M\text{-}SO_3\text{-}(CH_2)_a\text{-}S\text{-}(CH_2)_b\text{-}SO_3\text{-}M$;

(2) $M\text{-}SO_3\text{-}(CH_2)_a\text{-}O\text{-}CH_2\text{-}S\text{-}CH_2\text{-}O\text{-}(CH_2)_b\text{-}SO_3\text{-}M$;

(3) $M\text{-}SO_3\text{-}(CH_2)_a\text{-}S\text{-}S\text{-}(CH_2)_b\text{-}SO_3\text{-}M$;

(4) $M\text{-}SO_3\text{-}(CH_2)_a\text{-}O\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}O\text{-}(CH_2)_b\text{-}SO_3\text{-}M$;

(5) $M\text{-}SO_3\text{-}(CH_2)_a\text{-}S\text{-}C(=S)\text{-}S\text{-}(CH_2)_b\text{-}SO_3\text{-}M$;

(6) $M\text{-}SO_3\text{-}(CH_2)_a\text{-}O\text{-}CH_2\text{-}S\text{-}C(=S)\text{-}S\text{-}CH_2\text{-}O\text{-}(CH_2)_b\text{-}SO_3\text{-}M$;

(7) $A\text{-}S\text{-}(CH_2)_a\text{-}SO_3\text{-}M$; and

(8) $A\text{-}S\text{-}CH_2\text{-}O\text{-}(CH_2)_a\text{-}SO_3\text{-}M$;

wherein M is chosen from a hydrogen atom and an alkali metal; X is chosen from a hydrogen atom, an alkyl group containing 1 – 10 carbon atoms, an aryl group, a linear or cyclic amino group containing 1 – 6 nitrogen atoms, 1 – 20 carbon atoms, and multiple hydrogen atoms, or a hetero cyclic group containing 1 – 2 sulfur atoms, 1 – 6 nitrogen atoms, 1 – 20 carbon atoms, and multiple hydrogen atoms; and a and b are independently an integer of 3 – 8.

3. The method of claim 1, wherein the compound comprising the formula –X-S-Y- is present in the electrolytic copper plating solution in the range of 0.1 – 100 mg/L.

4. The method of claim 1 wherein a concentration of a compound comprising a structure of $-X\text{-}S^-$ in the electrolytic copper plating solution is controlled in the range of 1.0 μmol/L or lower.

5. The method of claim 1 wherein the substrate is chosen from a printed circuit board and a wafer.

6. The method of claim 1 wherein the substrate comprises through holes or via holes.

7. The method of claim 1 further comprising the steps of contacting the substrate with the electrolytic copper plating solution and applying sufficient current density to deposit copper on the substrate.

8. A method of treating an electrolytic copper plating solution comprising the step of contacting the electrolytic copper plating solution with ozone, wherein the electrolytic copper plating solution comprises a compound comprising the formula of –X-S-Y-, wherein X and Y are independently chosen from hydrogen atom, carbon atom, sulfur atom, nitrogen atom, and oxygen atom, and X and Y may be the same only when they are a carbon atom.